$C_3H_3^-$ and the slight total destabilization of CH_2CN^+ is to take into account the σ framework. Both groups C≡CH and CN are electron withdrawing (the later far more than the former) and thus stabilize anions and destabilize cations by inductive effect.

Therefore the σ effect seems to be more important than the π effect in determining the stability of the four species studied in this paper. In a general manner both π and σ interactions are more important for charged species compared to neutral species. Considering only one of these terms would lead to wrong conclusions especially if the contributions are in opposite directions as in CH_2CN^+.

Conclusion

This work shows the following trends: The geometrical parameters do not give sufficient information to describe a delocalized species: in particular they do not give the balance between the most important mesomeric structures. A valence-bond analysis is thus necessary.

There is no evident relation between the π charge distribution of delocalized charged species and the electronegativity of the β atoms. In fact, in anions, the first-order perturbation due to electronegativity (inductive effect) is opposed to the second-order effect, the repartition of the π charge (mesomeric effect). The prevalence of one effect over the other depends on the considered atom and the result is not simply foreseeable.

The most important feature is that there is no relationship between the π delocalization and the stability of the studied species. Firstly because the π delocalization does not represent the π stabilization for the anions and secondly because the σ effects can play a decisive role especially when a heteroatom substituent is present in the system. At this stage the conclusions are limited to these systems. Their generalization would need the study of some more species, which will be undertaken in the future.

Acknowledgment. The author is grateful to Prof. Nguyen Trong Anh, J. M. Lefour, and Drs. Y. Jean and S. Shaik for helpful discussions and advice.

Registry No. CH_2CN^+, 34430-18-7; CH_2CN^-, 21438-99-3; CH_2CCH^+, 21540-27-2; CH_2CCH^-, 31139-07-8.

Redox Behavior of Some New Bipyran and Bithiopyran Derivatives. One- vs. Two-Electron Oxidations

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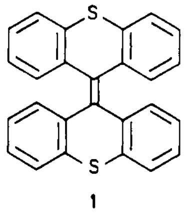
Three classes of $\Delta^{4,4'}$-4*H*-bipyran and -bithiopyran derivatives undergo either two unresolved one-electron oxidations, where $E_2°'$ may be more or less than $E_1°'$, or a single reversible two-electron oxidation, depending on molecular structure. The first class of compounds has one benzene ring fused to the pyran ring, and the second class consists of compounds with at least eight methylidene groups separating the heterocyclic rings. The third class contains compounds with the pyran or thiopyran rings separated by an ethanediylidene group that is substituted by at least one methyl or phenyl substituent. A rationale is proposed for the observed redox behavior.

Introduction

Electron donors exhibiting two reversible one-electron oxidation potentials are quite common.[1] In contrast, electron-donor molecules that exhibit the electrochemical behavior of a single two-electron reversible oxidation are rare.[2,3] This paper describes the synthesis and electrochemical behavior of a class of compounds whose redox behavior is controlled by steric interactions, the distance between the electroactive groups, and the nature of the heteroatom in some simple bipyran and thiopyran derivatives. $\Delta^{4,4'}$-4*H*-Bipyran and -bithiopyran derivatives normally exhibit two reversible one-electron oxidations.[1a,1h,3a-d] We set out to investigate the effect of structural changes on the separation between the first and second oxidation waves of these compounds. We found three distinct classes of pyrans and thiopyrans that exhibit a single reversible two-electron oxidation wave where $\Delta E°'$, i.e., $\Delta E°' = E_2°' - E_1°'$, may be positive, negative, or zero, depending on molecular structure.

Results and Discussion

The first class contains compounds with at least one benzene ring fused to the pyran nucleus. It has been reported that bithioxanthene (1) exhibits a single but irreversible two-electron oxidation at $E_p = +1.34$ V (vs. SCE, CH_2Cl_2).[4] The irreversibility is due to considerable structural and solvent reorganization between the charged and uncharged species.[4] We have shown that the related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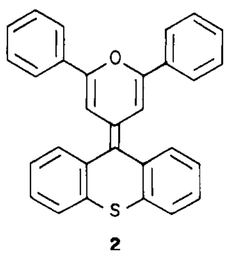
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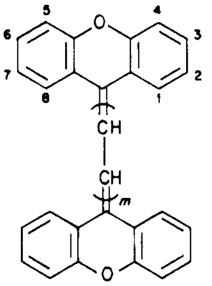
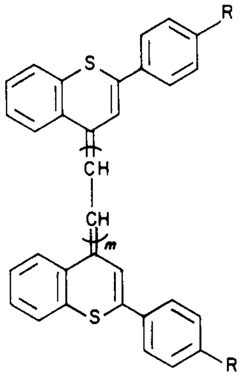
Table I. Oxidation Potentials of



compd	m		$E_1^{\circ\prime}$ $(n)^a$	E_pI $(n)^a$	$E_2^{\circ\prime}$ $(n)^a$	$\Delta E^{\circ\prime}$,^{b} mV
3	0			+1110 (2)		
4	0	3,4-benzo		+600 (2)		
5	1	3,4,5,6-dibenzo	+270 (1)		+570 (1)	+200
6	1	1,2,7,8-dibenzo	+780 (2)			+20

[a] Two-electron oxidation confirmed by coulometry [(n) = number of electrons transferred]. $E^{\circ\prime}$ is recorded in millivolts vs. the standard calomel electrode in methylene chloride solvent. [b] $\Delta E^{\circ\prime} = E_2^{\circ\prime} - E_1^{\circ\prime}$. The scan rate was 20 mV/s.

Table II. Oxidation Potentials of



compd	m	R	E_{pa},^{a} mV	E_{pc},^{a} mV	n^b	$\Delta E^{\circ\prime}$,^{c} mV
7	0	H	452	410	2	0
8	0	OCH_3	358	310	2	+18
9	1	H	533	458	2	+55

[a] E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, vs. the standard calomel reference electrode in methylene chloride solvent. [b] n = number of electrons transferred. [c] $\Delta E^{\circ\prime} = E_2^{\circ\prime} - E_1^{\circ\prime}$ (determined from Table II in ref 3e). The scan rate was 20 mV/s.

$\Delta^{4,9'}$-2,6-diphenyl-4-(thioxanthenyl)-4*H*-pyran (**2**) displays a single reversible oxidation at +0.50 V [vs. SCE (CH_2Cl_2)] which involves two electrons.[1a] We have continued our investigation of some xanthene derivatives, and the electrochemical data in Table I show the influence of fused benzene rings in selected examples.

Table II presents the oxidation potentials of some flavene and thioflavene dimers and related structures that also exhibit two closely spaced one-electron oxidation processes, except for compound **7**, which exhibits a single reversible two-electron oxidation potential. The redox behavior of **7** was consistent with the requirements outlined by Richardson and Taube[3e] in order to apply their method for determining the separation between redox couples. All of the oxygen analogues of the compounds in Table II gave two well-separated one-electron oxidations.[5] We attribute this difference in redox behavior to the greater aromatic stability of thiopyrylium vs. pyrylium.[6]

The redox behavior of **3**–**9** demonstrates the effect of the severe steric interactions in the xanthene and flavene dimers. The one-electron oxidation of the dimer to give a cation radical should diminish the double bond character of the bond between the heterocyclic rings and allow the two halves of the dimer to twist out of planarity. It is expected that the second-electron oxidation of the twisted form takes place at approximately the same potential as the initial oxidation. A similar explanation was used for the two-electron reduction of bianthrone.[7] Steric interactions do not seem to explain the behavior of compound **9**, which contains a spacer between the rings, but a comparison of the potentials obtained for **5** and **6** confirms the importance of steric interactions, i.e., $\Delta E^{\circ\prime}$ is positive for **6**, **8**, and **9** and zero for **7**.

The second class of dimers was synthesized to verify literature observations that separating the pyran or thiopyran rings by an extended conjugated chain would lead to a gradual decrease in the separation of the two one-electron oxidation potentials until they coalesce. We have shown that eight methylidene groups are needed to make $\Delta E^{\circ\prime} \sim 0$.[8] All the compounds listed in Table III undergo a single unresolved redox couple, which corresponds to a transfer of two electrons, as determined by coulometry.

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(6) (a) Yoneda, S.; Sujimoto, T.; Tanaka, O.; Moriya, Y.; Yoshida, Z. *Tetrahedron* **1975**, *31*, 2669. (b) Tolmachev, A. I.; Kornilov, M. Yu.; Shulezhko, L. M.; Turov, A. V. *Teor. Eksp. Khim.* **1975**, *11*, 556. (c) Sandman, D. J.; Holmes, T. J.; Warner, D. E. *J. Org. Chem.* **1979**, *44*, 880.

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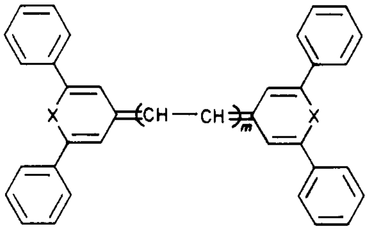
Table III. Oxidation Potentials of



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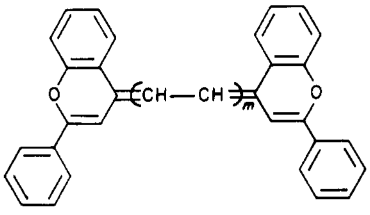
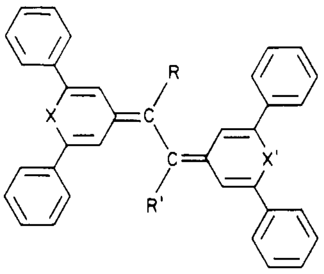


B

compd	structure	X	m	E_{pa},[a] mV	E_{pc},[a] mV	n[b]	$\Delta E^{\circ\prime}$,[c] mV
10	A	O	4	+190	+150	2	-10
11	A	S	4	+230	+190	2	-10
12	B		4	+370	+320	2	+20
13	A	S	6	+220	+170	2	+20
14	B		6	+290	+260	2	-100

[a] E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, vs. the standard calomel reference electrode. [b] n = number of electrons transferred. [c] $\Delta E^{\circ\prime} = E_2^{\circ\prime} - E_1^{\circ\prime}$ (determined from Table II in ref 3e). The scan rate was 20 mV/s.

Table IV. Oxidation Potentials of C



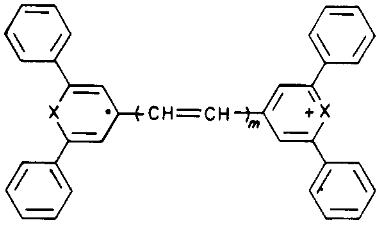
C

X(X') = O or S

compd	X′	X	R	R′	E_{pa},[a] mV	E_{pc},[a] mV	n[b]	$\Delta E^{\circ\prime}$,[c] mV
15	S	S	CH_3	CH_3	320	270	2	20
16	O	O	CH_3	CH_3	170	140	2	-200
17	S	S	C_6H_5	C_6H_5	400	340	2	38
18	O	O	C_6H_5	C_6H_5	420	320	2	70
19	S	S	H	CH_3	320	260	2	38
20	O	O	H	CH_3	230	160	1	140
					370	310	1	
21	O	S	H	CH_3	280	215	1	80
					360	300	1	

[a] E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, vs. the standard calomel reference electrode. [b] n = number of electrons transferred. [c] $\Delta E^{\circ\prime} = E_2^{\circ\prime} - E_1^{\circ\prime}$ (determined from Table II in ref 3e). The scan rate was 20 mV/s.

We postulate that the existence of closely spaced $E^{\circ\prime}$ values for these compounds is due to the large separation between the cation and radical sites formed after one-electron oxidation. In other words, the removal of the second electron occurs at approximately the same potential as removal of the first electron, owing to less coulombic repulsion in the dication in systems with large separation between electroactive moieties, as shown below for the cation radical of system A. Compounds **10**, **11**, and **14** exhibit $\Delta E^{\circ\prime}$ values that are negative in sign, indicating that $E_2^{\circ\prime}$ occurs at less anodic potentials than $E_1^{\circ\prime}$. Compounds **12** and **13** both exhibit $\Delta E^{\circ\prime}$ of 20 mV.



The third class of dimers that exhibit a single redox wave, which corresponds to the stepwise transfer of two electrons, is shown in Table IV. This class of dimers is represented by structure C in which R and R′ are methyl or phenyl or R is hydrogen and R′ is methyl. Compounds **19**, **20**, and **21** demonstrate that the heteroatom plays a role in determining the relative potentials of $E_1^{\circ\prime}$ and $E_2^{\circ\prime}$. All of the compounds in Table IV except for **16** exhibit positive values of $\Delta E^{\circ\prime}$.

The reason for the redox behavior of **15**–**21** is not known, but we suggest that a steric interaction as well as the heteroatom determines the electrochemical behavior similar to that found for **3**–**9**.

Synthesis. The synthesis of most of the dimers was by published procedures (see Experimental Section). Two examples, **5** and **6**, could not be prepared by our standard procedure (treating the methylpyrylium salt with pyridine),[9,10] owing to the formation of stable methylene bases; **5** and **6** were synthesized as shown in Scheme I.

Because **16**–**18** could not be prepared by the cupric perchlorate oxidation described in Scheme I, we resorted

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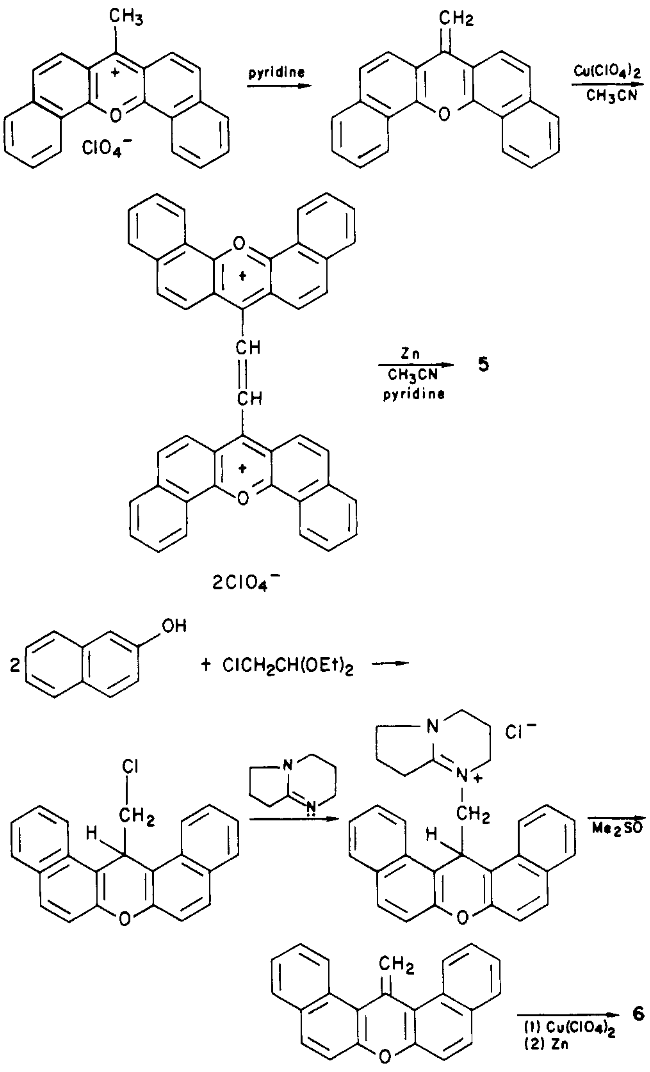
(9) Van Allan, J. A.; Reynolds, G. A. *Tetrahedron Lett.* **1969**, 2047.
(10) Reynolds, G. A.; Van Allen, J. A. *J. Heterocycl. Chem.* **1969**, *6*, 623.

Scheme I



to controlled-potential electrolysis of the corresponding methylene bases prepared independently or in situ. The electrodimerization reactions take place via the methylene-base cation radicals, which then lose two protons to form **15**–**18**, as shown in Scheme II.

Experimental Section

General Methods. Melting points were determined with a Mel-Temp apparatus and are uncorrected. The cyclic voltammetric measurements were made on a Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer in the standard three-electrode configuration. A platinum inlay electrode was used as the working electrode along with a platinum auxiliary electrode and a standard calomel electrode (SCE). The electrolyte was 0.1 M tetrabutylammonium fluoroborate (TBAF) recrystallized from ethyl acetate/pentane, and the solvent was methylene chloride. The redox behavior of the pyrans listed in Tables I–IV was independent of scan rate below 50 mV/s. The effect of solvent on the redox properties was not investigated. Coulometry was performed on a Princeton Applied Research Model 179 digital coulometer. Coulometry (constant potential electrolysis) of 10^{-4} M solutions was used to determine the number of electrons transferred. The compounds studied fulfill the requirements outlined by Taube and Richardson[3e] in order to apply their method of determining $\Delta E^{\circ\prime}$. Every compound studied exhibited reversible electron-transfer behavior at the working electrode surface. Combustion analyses were performed by the Analytical Sciences Division of the Kodak Research Laboratories.

Materials. Compounds **3** and **4** were prepared from 9*H*-xanthene-9-thione or the 3,4-benzo derivative and copper powder in refluxing xylene.[11] Compound **4** was obtained in 63% yield: mp 349–350 °C.

7,7′-(Ethane-1,2-diylidene)bis[[7*H*]dibenzo[*c*,*h*]xanthene] (5). A suspension of 6.0 g (0.02 mol) of 7*H*-dibenzo[*c*,*h*]xanthen-7-one[12] in 50 mL of dry tetrahydrofuran (THF) was stirred, and 15 mL of 2.8 M methylmagnesium chloride in THF was added. The clear solution was heated at 60 °C for about 15 min, and a solid separated. The mixture was chilled in an ice bath, and ice and hydrochloric acid were added, followed by 6 mL of 70% perchloric acid. The yellow solid was collected, washed with water, and dried, yielding 7.0 g of 7-methyldibenzo[*c*,*h*]xanthylium perchlorate: mp 250–251 °C (lit.[13] mp 263–264 °C). A solution of 10 g of the xanthylium salt in 30 mL of pyridine was refluxed for 10 min, diluted with 30 mL of methyl alcohol, and cooled, and the 7-methylenedibenzo[*c*,*h*]-7*H*-xanthene was collected: yield 7 g (93%); mp 181–182 °C (lit.[13] mp 181 °C). A mixture of 1.6 g of the methylene compound, 6.4 g of $Cu(ClO_4)_2\cdot 9H_2O$, and 25 mL of acetonitrile was refluxed for 30 min and cooled, and the bisxanthylium salt **22** was collected: yield 1.7 g (80%); mp 250 °C (explodes). A suspension of 3.0 g of **22** in 60 mL of acetonitrile and 6 mL of pyridine was treated with 1.5 g of granular zinc, and the mixture was stirred for 1 h. The solid was collected, dissolved in hot pyridine, and filtered, and the filtrate was diluted with methyl alcohol. The solution was chilled and **5** was collected: yield 1.8 g; mp 384–386 °C; field-desorption mass spectrum, *m/e* 586; electron-impact mass spectrum, *m/e* 586 (100%), 305 (11%), 293 (27%), and 281 (12%).

Anal. Calcd for $C_{44}H_{26}O_2$: C, 90.1; H, 4.5. Found: C, 89.9; H, 4.7.

14,14′-(Ethane-1,2-diylidene)bis[[14*H*]dibenzo[*a*,*j*]xanthene] (6). A solution of 14.4 g (0.1 mol) of 2-naphthol and 6.2 mL (0.05 mol) of diethyl chloracetal in 20 mL of chloroform and 6 mL of concentrated hydrochloric acid was refluxed for 4 h. Ethyl alcohol (40 mL) was added, and reflux was continued for 30 min. After cooling, the white crystals were collected, yielding 12 g of 14-(chloromethyl)-14*H*-dibenzo[*a*,*j*]xanthene: mp 177–178 °C (lit.[14] mp 174 °C). A solution of 2.0 g (6 mmol) of the chloromethyl compound and 2.0 mL of diazabicyclononene in 10 mL of toluene was refluxed for 1 h and cooled to room temperature. The toluene was decanted from a viscous oil, and the oil was dissolved in ethyl alcohol. Perchloric acid was added to this solution, giving 1.8 g of 14-[(1,5-diazabicyclo[4.3.0]non-5-ene)methyl]-14*H*-dibenzo[*a*,*j*]xanthene perchlorate: mp 186 °C dec.

Anal. Calcd for $C_{29}H_{27}ClN_2O_5$: C, 67.1; H, 5.2; N, 5.4. Found: C, 66.9; H, 5.8; N, 5.2.

A solution of 1.8 g of the perchlorate and 10 mL of dimethyl sulfoxide was refluxed for 30 min, diluted with 75 mL of methyl alcohol, and cooled, giving 1.0 g of 14-methylene-14*H*-dibenzo-[*a*,*j*]xanthene: mp 152–154 °C (lit.[15] mp 154 °C).

A solution of 2.9 g (0.01 mol) of the methylene compound, 9.6 g of $Cu(ClO_4)_2\cdot 9H_2O$, and 150 mL of acetonitrile was heated on a steam bath for 30 min and allowed to stand overnight. The red crystals were collected, washed with dilute hydrochloric acid, and air dried, yielding 2.7 g of 14,14′-(1,2-ethylene)bisdibenzo[*a*,*j*]xanthylium perchlorate: mp 288 °C explodes.

Anal. Calcd for $C_{44}H_{26}Cl_2O_{10}$: C, 67.4; H, 3.3; Cl, 9.0. Found: C, 67.6; H, 3.6; Cl, 8.9.

A suspension of 3.0 g of the bisxanthylium salt in 60 mL of acetonitrile was stirred, and 6 mL of pyridine and 1.5 g of granulated zinc were added. The mixture was stirred for 1 h, diluted with 30 mL of methyl alcohol, and chilled, and the solid was collected. Recrystallization from pyridine/methyl alcohol gave 1.8 g of **6**: mp 384–386 °C.

Anal. Calcd for $C_{44}H_{26}O_2$: C, 90.1; H, 4.5. Found: C, 90.2; H, 4.7.

Preparation of 7–13. Compounds **7** and **8** were prepared by Schonberg's procedure.[11] Compound **7** was obtained in 78% yield (mp 298–299 °C) and **8** in 52% yield (mp 274–275 °C). Compound **9** was obtained in 41% yield (mp 278–279 °C) from 4-methyl-

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[11] Schonberg, A.; Schutz, O.; Nickel, S. *Chem. Ber.* **1928**, *61*, 1375.

[12] Van Allan, J. A.; Stenberg, J. F.; Reynolds, G. A. *J. Heterocycl. Chem.* **1979**, *16*, 1663.

[13] Kamel, M.; Shoeb, H. *Tetrahedron* **1964**, *20*, 483.

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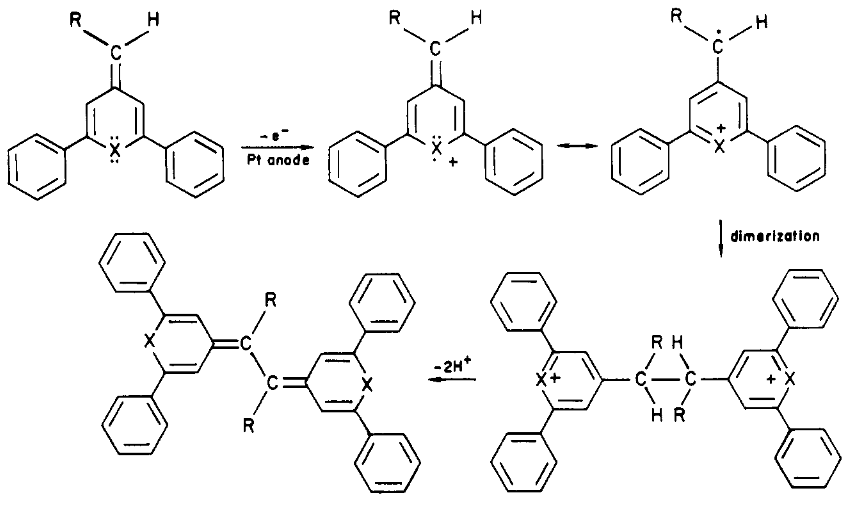
[15] Wizinger, R.; Alatar, Y. *Helv. Chim. Acta* **1947**, *30*, 189.

Scheme II[a]



[a] R = CH_3, C_6H_5; X = O, S.

thioflavylium perchlorate and pyridine as described for the oxygen analogue.[9]

The syntheses of compounds **9**–**13** have been described.[8]

2,2′,6,6′-Tetraphenyl-4,4′-(butane-2,3-diylidene)bis[4*H*-thiopyran] (15). A mixture of 0.50 g of 2,6-diphenyl-4-ethylthiopyrylium perchlorate and 2 mL of pyridine was heated on a steam bath for 2 h and chilled, and the solid was collected. The product was recrystallized from toluene, giving 0.12 g of pale yellow needles: mp 231–232 °C; field-desoprtion mass spectrum, *m/e* 550 ($C_{38}H_{30}S_2$); NMR ($CDCl_3$) δ 1.95 (s, 6 H, CH_3), 6.62 and 6.85 (s, 4 H, thiopyran), 7.20–7.70 (m, 20 H, arom).

2,2′,6,6′-Tetraphenyl-4,4′-(butane-2,3-diylidene)bis[4*H*-pyran] (16). Because the method described for preparing **15** did not work with 2,6-diphenyl-4-ethylpyrylium perchlorate, **16** was synthesized electrochemically as follows.

The methylene base of 2,6-diphenyl-4-ethylpyrylium perchlorate exists in equilibrium with the pyrylium salt in acetonitrile containing tetrabutylammonium fluoroborate (TBAF) (0.1 M). We electrochemically oxidized the methylene base by dissolving the pyrylium salt (0.50 g) in 100 mL of acetonitrile containing the TBAF electrolyte, purging the reaction mixture with argon, and applying a potential of +0.7 V (vs. SCE) until one electron equivalent was removed. The reaction was monitored by cyclic voltammetry and determined to be complete when the solution exhibited a reversible redox wave centered at +0.15 V with ~45 mV peak separation and the irreversible anodic wave at ~0.72 V was no longer present. The acetonitrile solution was flash evaporated, and the product was dissolved in methylene chloride and chromatographed on silica gel to remove the electrolyte. The product was not stable to chromatography and evidently oxidized to colored compounds. We observed similar behavior for other bipyran dimers. The cyclic voltammetry data were obtained for the unisolated material.

2,2′,6,6′-Tetraphenyl-4,4′-(1,2-diphenyl-1,2-ethanediylidene)bis[4*H*-thiopyran] (17). To a suspension of 1.45 g of 4-benzyl-2,6-diphenylthiopyrylium perchlorate in 25 mL of CH_2Cl_2 was added 1 mL of triethylamine. The solid rapidly dissolved. The solution was washed with water and dried ($MgSO_4$), and the solvent was evaporated. The residue was recrystallized from toluene, giving 1.2 g of 4-benzylidene-2,6-dipenyl-4*H*-thiopyran: mp 139–140 °C; NMR ($CDCl_3$) δ 6.68 (s, 1 H), 6.68 (s, 1 H), 7.19 (s, 1 H), 7.2–7.5 (m, 15 H). A solution of 4-benzylidene-2,6-diphenyl-4*H*-thiopyran (0.50 g) in 100 mL of methylene chloride containing TBAF (0.1 M) electrolyte was electrolyzed at +0.83 V by constant-potential electrolysis until one electron equivalent was removed. The reaction mixture was purged with argon before and during the reaction. The reaction was determined to be complete by cyclic voltammetry, which showed the appearance of a reversible redox couple centered at 0.37 V and the disappearance of the oxidation wave at +0.83 V. The methylene chloride solution was flash evaporated, and the TBAF was dissolved in 50 mL of methanol, giving 0.45 g of crystalline product after suction filtration. Recrystallization from isopropyl alcohol gave 60 mg of **17**: mp 130–132 °C; mass spectrum (FD), *m/e* 674 ($C_{48}H_{34}S_2$).

Anal. Calcd for $C_{48}H_{34}S_2$: C, 85.4; H, 5.1; S, 9.5. Found: C, 85.2; H, 5.2; S, 9.3.

2,2′,6,6′-Tetraphenyl-4,4′-(1,2-diphenyl-1,2-ethanediylidene)bis[4*H*-pyran] (18). A mixture of 1.0 g of 4-benzyl-2,6-diphenylpyrylium perchlorate, 0.5 mL of triethylamine, and 25 mL of CH_2Cl_2 was stirred until the solid dissolved and worked up as described for the thio analogue, giving 0.70 g of 4-benzylidene-2,6-diphenyl-4*H*-pyran: mp 133–134 °C.

A solution of 4-benzylidene-2,6-diphenyl-4*H*-pyran (0.50 g) in 100 mL of methylene chloride containing TBAF (0.1 M) electrolyte was electrolyzed at +1.4 V until one electron equivalent was removed. The reaction mixture was purged with argon before and during the reaction. The reaction was shown to be complete by cyclic voltammetry, with the appearance of a two-electron redox couple centered at +0.37 V and the disappearance of the irreversible anodic wave at ~+1.4 V. The methylene chloride solution was flash evaporated, and the TBAF was dissolved in 50 mL of methanol, giving 0.42 g of crystalline product after suction filtration. Recrystallization from isopropyl alcohol with a small amount of toluene gave 165 mg of **18**: mp 255–256 °C; mass spectrum, *m/e* 642 ($C_{48}H_{34}O_2$).

Anal. Calcd for $C_{48}H_{34}O_2$: C, 89.7; H 5.3. Found: C, 89.5; H, 5.4.

2,2′,6,6′-Tetraphenyl-4,4′-(propane-1,2-diylidene)bis[4*H*-thiopyran] (19) and 2,6-Diphenyl-4-[2-(2,6-diphenyl-4*H*-pyran-4-ylidene)propan-1-ylidene]-4*H*-thiopyran (21). To a stirred solution of 300 mg (2 mmol) of dry potassium *tert*-butoxide[16] in 25 mL of dry THF under argon in a 3-heptanone/dry ice cooling bath (-35 °C) was added a cooled solution of 332 mg of 2,6-diphenyl-4-(trimethylsilyl)-4*H*-thiopyran[17] (1 mmol) in 10 mL of dry THF via syringe (a light green color usually appeared upon addition). With the internal temperature kept slightly below -20 °C, 0.95 mL (2 mmol) of *n*-BuLi (2.1 M in hexane) was added dropwise via syringe, and the reaction mixture was stirred for 30 min.

To the mixture was added 608 mg of 2,6-diphenyl-4-(1-formylethylidene)-4*H*-thiopyran (2 mmol) at -35 °C, giving **19**, or 576 mg of 2,6-diphenyl-4-(1-formylethylidene)-4*H*-pyran (2 mmol) at -35 °C, giving **21**. 30 min after the addition, the reaction mixture was allowed to equilibrate to room temperature for 30 min, poured into 400 mL of 5% aqueous NH_4Cl, and stirred for 1 h. The precipitate was collected, washed with water, dried in air, and purified by recrystallization from 50 mL of dry methanol, giving the desired product.

For **19** (375 mg, 70%): mp 104–105 °C; FD mass spectrum, *m/e* 536 (M^+ for $C_{20}H_{16}S_2$); NMR ($CDCl_3$) δ 2.03 (s, 3 H), 5.95

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[16] Dry powdered potassium *tert*-butoxide (alcohol free) was purchased from MSA Research Corp.

[17] Chen, C. H.; Doney, J. J.; Reynolds, G. A. *J. Org. Chem.* **1982**, *47*, 680.

(s, 1 H), 6.80–7.00 (m, 4 H), 7.20–7.70 (m, 20 H).

Anal. Calcd for $C_{37}H_{28}S_2$: C, 82.8; H, 5.3. Found:[18] C, 81.3; H, 5.2.

For **21** (300 mg, 58%): mp 170–172 °C; FD mass spectrum, *m/e* 520 (M^+ for $C_{20}H_{16}OS$); NMR ($CDCl_3$) δ 2.05 (s, 3 H), 5.95 (s, 1 H), 6.55 (m, 2 H), 6.70 (m, 2 H), 7.20–7.80 (m, 20 H).

Anal. Calcd for $C_{37}H_{28}OS$: C, 85.4; H, 5.4. Found: C, 85.0; H, 5.4.

2,2′,6,6′-Tetraphenyl-4,4′-(propane-1,2-diylidene)bis[4*H*-pyran] (20). A mixture of 1.7 g (5 mmol) of 2,6-diphenylpyrylium perchlorate in 50 mL of dry THF was stirred under argon and chilled in a dry ice/acetone bath, and 2.6 mL (5 mmol) of 1.9 M sodium ethyl ethylphosphonate[19] was added. The mixture was stirred until a clear solution was obtained. To the solution was added 3.0 mL (5 mmol) of 1.6 M *n*-butyllithium. The solution was stirred for 5 min, and 1.4 g (5 mmol) of 2,6-diphenyl-4-(1-formylethylidene)-4*H*-pyran was added, and the mixture was stirred while it warmed to room temperature. The mixture was allowed to stand overnight and evaporated to dryness, and the residue was dissolved in CH_2Cl_2 and passed through a short column of alumina eluted with CH_2Cl_2. The solvent was removed, and the residue was recrystallized from toluene, giving 0.85 g of **20**: mp 196–197 °C; FD mass spectrum, *m/e* 504 (M^+).

Anal. Calcd for $C_{37}H_{28}O_2$: C, 88.1; H, 5.6; S, 6.3. Found: C, 87.8, H, 5.3; S, 6.7.

Registry No. **3**, 517-45-3; **4**, 92762-56-6; **5**, 92786-66-8; **6**, 92762-57-7; **7**, 92762-58-8; **8**, 92762-59-9; **9**, 24258-21-7; **10**, 86393-16-0; **11**, 86393-17-1; **12**, 86393-23-9; **13**, 86393-19-3; **14**, 86393-24-0; **15**, 92762-60-2; **16**, 92762-61-3; **17**, 92762-62-4; **18**, 92762-63-5; **19**, 92762-65-7; **20**, 92762-64-6; **21**, 80160-67-4; **22**, 92762-68-0; CH_3Cl, 74-87-3; $Cu(ClO_4)_2$, 13370-18-8; $ClCH_2CH(OEt)_2$, 621-62-5; EtP(O)OEt(ONa), 34326-12-0; 7*H*-dibenzo[*c,h*]xanthen-7-one, 3264-24-2; 7-methyldibenzo[*c,h*]xanthylium perchlorate, 37399-98-7; 7-methylenedibenzo[*c,h*]-7*H*-xanthene, 92762-66-8; 2-naphthol, 135-19-3; 14-(chloromethyl)-14*H*-dibenzo[*a,j*]xanthene, 72138-26-2; diazabicyclononene, 3001-72-7; 14-[(1,5-diazabicyclo[4.3.0]non-5-enyl)methyl]-14*H*-dibenzo[*a,j*]xanthene perchlorate, 92762-70-4; 14-methylene-14*H*-dibenzo[*a,j*]xanthene, 6612-09-5; 14,14′-(1,2-ethylene)bisdibenzo[*a,j*]xanthylium perchlorate, 92762-72-6; 2,6-diphenyl-4-ethylthiopyrilium perchlorate, 86393-26-2; 2,6-diphenyl-4-ethylidene-4*H*-thiopyran, 21186-87-8; 4-benzyl-2,6-diphenylthiopyrilium perchlorate, 41786-21-4; 4-benzylidene-2,6-diphenyl-4*H*-thiopyran, 41786-16-7; 4-benzyl-2,6-diphenylpyrilium perchlorate, 1252-67-1; 4-benzylidene-2,6-diphenyl-4*H*-pyran, 1168-63-4; 2,6-diphenyl-4-(trimethylsilyl)-4*H*-thiopyran, 80160-61-8; 2,6-diphenyl-4-(1-formylethylidene)-4*H*-thiopyran, 92762-73-7; 2,6-diphenylpyrilium perchlorate, 3558-68-7; 2,6-diphenyl-4-(1-formylethylidene)-4*H*-pyran, 40564-75-8.

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[18] Repeated attempts to obtain a satisfactory combustion analysis for **21** were unsuccessful.

[19] Commercially available from Organometallics Inc., East Hampstead, New Hamphire.

Novel $LiAlH_4$ Reduction Pathway. Reactions of 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones with $LiAlH_4$. Preparations of 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazoles and Side Products

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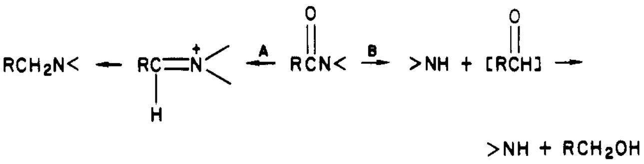
The direct $LiAlH_4$ reduction of 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones, **2**, to 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazoles, **10**, was unsuccessful. When the amide **2** had an *N*-phenyl substituent the reduction gave an *N*-carbonyl cleavage followed by carbonyl reduction to amino alcohols **6a–d**. When the amide **2** had *N*-methyl, *N*-*tert*-butyl, or *N*-2,6-dimethylphenyl as a substituent, then cleavage yielded an unusual formamide product, **9e–i**. Further $LiAlH_4$ treatment of **9e–h** gave **10e–h** by reductive ring closure of the iminium zwitterion **11e–f**, **14g**, or **14h** by addition of hydride to the intermediate **11g** or **11h** and/or carbonyl cleavage to **13e** or **13f**. $LiAlH_4$ treatment of **9i** gave only **13i**. Dehydrative ring closure of compounds **6a** and **6b** with P_2O_5 gave the products **10a** and **10b**.

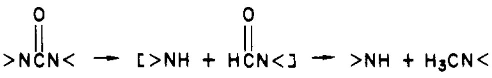
The reduction of amides with lithium aluminum hydrides ($LiAlH_4$) is a frequently employed reaction. The most usual pathways are depicted in Scheme I. Path A involves the conversion of the amide to an iminium ion followed by the subsequent reduction of the iminium ion to the corresponding amine.[1] This is the most common pathway. The second pathway generally encountered[2] involves hydride attack on the carbonyl followed by the formation of aldehydic and amine moieties with the aldehydic portion being further reduced to alcohol (path B).

A slight variation on pathway B is encountered in the $LiAlH_4$ reduction of substituted ureas[3] where one still finds a carbonyl–nitrogen amide linkage cleavage (Scheme II) followed by reduction of the formyl group to a methyl.

Scheme I



Scheme II



In a previous paper we described a new synthesis of 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones, **2**, by the

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[1] (a) Moffett, R. B. "Organic Synthesis"; Wiley: New York, 1963; Collect Vol. IV, p 354. (b) Cope, A. C.; Ciganek, E. Ibid. p 339. (c) Takayama, K.; Isube, M.; Harano, K.; Taguchi, T. *Tetrahedron Lett.* **1973**, 365. (d) Moos, W. H.; Gless, R. D.; Rapoport, H. *J. Org. Chem.* **1982**, *47*, 1831 and references cited in all of the above.

[2] (a) Nahm, S.; Weinreb, S. N. *Tetrahedron Lett.* **1981**, *22* [39], 3815. (b) Staab, H. A.; Braunling, H. *Liebigs Ann. Chem.* **1962**, *654*, 119. (c) Brown, H. C.; Tsukamoto, A. *J. Am. Chem. Soc.* **1961**, *83*, 4549.

[3] (a) Lehmann, J.; Kraft, G. *Arch. Pharm.* (*Weinheim, Ger.*) **1982**, *315* [11], 967; *Chem. Abstr.* **1983**, *98*, 16647a. (b) Kashima, C.; Katoh, A.; Yoshiwara, N.; Omote, Y. *J. Heterocycl. Chem.* **1981**, *18*, 1595.